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COMPLETE SPECIFICATION

Process for the Treatment of Vinyl Chloride Polymers

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for treating vinyl chloride polymers.

According to the present invention, there is provided a process which consists in that vinyl chloride polymers are mixed with copolymers from ethylene and vinyl esters and with radical-forming substances and then heated at temperatures of 50 to 200°C during or after moulding.

The term vinyl chloride polymers also comprises, in the present case, copolymers of vinyl chloride with other vinyl compounds, for example, with vinyl esters, such as vinyl acetate, or also with vinylidene chloride. The polymers can be produced in any way, for example, by the emulsion or suspension method; the degree of their polymerisation may lie within a wide range, polymers with K-values of 50 to 80 having proved to be especially advantageous.

The vinyl chloride polymers should expediently contain plasticisers, for example esters of phthalic acid, such as dioctyl phthalate, dibutyl phthalate or dinonyl phthalate, esters of phosphoric acid, such as tricresyl phosphate, or esters of sebacic acid and adipic acid, such as dioctyl sebacate and dibutyl adipate. Depending upon the intended purpose of processing or use, the vinyl chloride polymers may also contain further additives, such as stabilisers, lubricants, fillers, wood powder and glass fibers, as well as dyestuffs and pigments. An addition of basic substances, especially metal oxides, such as magnesium oxide, has also proved useful in many cases.

Examples of copolymers of ethylene and viynl esters are the copolymers of ethylene with vinyl acetate, vinyl propionate, vinyl stearate and/or vinyl benzoate. They can be produced by any desired method, for example, according to the process of British Patent Specification No. 843,974. The proportion of ethylene to vinyl esters may vary within wide limits, for example between 20 to 80 parts of ethylene, on the one hand, and 80 to 20 parts of vinyl esters, on the other hand.

Suitable mixing proportions between the vinyl chloride polymers and the ethylene/vinyl ester copolymers can easily be ascertained by preliminary experiments. In general, it is advisable to use 5 to 50 parts by weight of ethylene/vinyl ester copolymer per 100 parts by weight of vinyl chloride polymer.

Examples of radical-forming substances are the esters of azo-dicarboxylic acid, furthermore peroxides, such as benzoyl peroxide, dichlorobenzoyl peroxide, *tert.*-butyl hydroperoxide, di-*tert.*-butyl peroxide, peroxy-dicarbonates, polymeric phthalyl peroxide, adipic acid - bis - *tert.* - butylperester, 2,5 - bis - (*tert.*- butylperoxy) - 2,5 - dimethyl - hexane or dicumyl peroxide. They are generally used in an amount of 0.2 to 10 parts by weight, referred to 100 parts by weight of ethylene/vinyl ester copolymer.

In many cases, it is expedient to add to the mixtures of vinyl chloride polymers,

ethylene/vinyl ester copolymers and radical-forming substances and also minor amounts of monomeric polymerisable compounds containing two or more olefinic double bonds, for example, triallyl cyanurate or triallyl phosphate, preferably in amounts of 0.5 to 10 parts by weight, referred to 100 parts by weight of ethylene/vinyl ester copolymer.

In order to mix the components concerned, the devices customary in industry can be used, for example kneaders or mixing rolls.

The time and temperature required for heating the mixtures depend upon the thermal stability and the rate of decomposition of the radical-forming substances. In general, the temperature lies between 50 and 200°C. with a heating period of between 60 minutes and 5 seconds.

The vinyl chloride polymers treated according to the process of the present invention offer a number of advantages over untreated vinyl chloride polymers. They do not become sticky when heated and do not stick to hot surfaces; mouldings produced from the treated vinyl chloride polymers can, therefore, be removed from the mould after shaping while hot, whereas mouldings from untreated vinyl chloride polymers necessitate cooling of the moulds before removal of the polymers. Furthermore, the vinyl chloride polymers treated by the process according to the present invention are no longer plastic at elevated temperatures, but elastic; furthermore, they exhibit an improved stability to organic solvents. The process of the present invention can, therefore, be used with advantage for the production of tubes, profiles or cable sheathings.

The process according to the present invention, it is of special importance for the production of coatings, for example, on textiles, fleeces, paper, leather, artificial leather, wood and metals. The procedure for this purpose may be such that the mixtures concerned are applied in the form of solutions, dispersions or foils to the substrates possibly provided with adhesives, followed, after removal of the solvent or dispersing agent, by heating, expediently with compression shaping.

The following Examples are given for the purpose of illustrating the present invention, the parts given being parts by weight:—

EXAMPLE 1:

100 parts polyvinyl chloride (produced by the suspension method: K-value 65) 20 parts ethylene/vinyl acetate copolymer (produced from 52 parts of ethylene and 48 parts of vinyl acetate: Mooney plasticity ML4'-100° C:25) 100 parts dioctyl phthalate, 1 part basic lead sulphate, and 10 parts magnesium oxide are mixed with one another on mixing rolls at 160°C, for 5 minutes. To the homogeneous mixture, there are subsequently added on a roller, heated to about 40°C., 1 part stearic acid, 25 parts highly-active, precipitated silic acid, 3 parts iron oxide, 3 parts dibenzoyl peroxide, and 3 parts triallyl cyanurate.

The mixture thus obtained is then stretched to a foil, the foil is applied to chrome-tanned skivers and heated at 120°C. in a press under a pressure of 2 kg/cm² for 10 Minutes. The coating thus formed can be released while hot; it is no longer thermoplastic.

EXAMPLE 2:

100 parts of a polymer with K-value 55, prepared from 85 parts vinyl chloride and 15 parts vinyl acetate by the emulsion method, 40 parts ethylene/vinyl acetate copolymer (prepared from 30 parts ethylene and 70 parts vinyl acetate; Mooney plasticity ML4'-100°C:15); 50 parts dioctyl phthalate, 1 part basic lead sulphate and 10 parts magnesium oxide are mixed with one another in an internal mixer at 160°C. for 5 minutes. To the homogeneous mixture there are subsequently added on a roller, heated to about 60°C. 1 part stearic acid, 20 parts highly-active silicic acid, 2 parts dicumyl peroxide and 3 parts triallyl cyanurate.

The mixture thus obtained is then injection-moulded and heated at 150°C. for 15 minutes in a compression mould under a pressure of 5 kg/cm². The profile thus obtained can be removed from the mould while hot; it shows a very good resilience under compressive stress at room temperature, as well as at 70°C.

EXAMPLE 3:

100 parts of a polymer of K-value 50, prepared from 80 parts of vinyl chloride and 20 parts of vinylidene chloride by the emulsion method, 20 parts of an ethylene/vinyl propionate copolymer (prepared from 65 parts of ethylene and 35 parts of vinyl propionate; Mooney plasticity ML4'-100°C:25) 100 parts of an ester from phenol and a paraffin-sulphonic acid chloride containing about 15 carbon atoms, 2 parts basic lead carbonate and 25 parts magnesium oxide are mixed with one another on mixing rolls at 160°C. for 5 minutes. To the homogeneous mixture, there are subsequently added on a roller, heated to about 40°C., 1 part stearic acid, 25 parts precipitated silicic acid, 3 parts 2,5 - bis - (*tert.* - butylperoxy) - 2,4 - di - methyl-hexane, and 3 parts triallyl phosphate. The mixture thus obtained is then stretched to a foil, placed on a cotton fabric and heated at 150°C. for 15 minutes in a press under a pressure of 3 kg/cm². A non-thermoplastic leather cloth is thus obtained which can be removed while hot.

WHAT WE CLAIM IS:—

1. A process for the treatment of vinyl

chloride polymers and copolymers, which consists in that vinyl chloride polymers or copolymers are mixed with copolymers from ethylene and vinyl esters and with radical-forming substances, and then heated at temperatures of 50 to 200°C. during or after moulding.

2. A process according to claim 1, wherein the vinyl chloride polymers or copolymers used have a k-value of 50 to 80.

3. A process according to Claim 1 or 2, wherein 5 to 50 parts by weight of ethylene-vinyl ester copolymer are used for 100 parts by weight of vinyl chloride polymer or copolymer.

4. A process according to any of the preceding claims, wherein 0.2 to 10 parts by weight of radical forming substances are used for 100 parts by weight of ethylene-vinyl ester copolymer.

5. A process according to any of the preceding claims, wherein there is additionally used a minor amount of monomeric polymerisable compounds containing two or more olefinic double bonds.

6. A process according to claim 5, wherein the additional polymerisable compound is used in an amount of 0.5 to 10 parts by weight per 100 parts by weight of ethylene-vinyl ester copolymer.

7. A process according to any of the preceding claims, wherein the treatment is carried out for a period of 60 minutes to 5 seconds at a temperature between 50 and 200°C.

8. A process according to claim 1 for the treatment of vinyl chloride polymers and copolymers, substantially as hereinbefore described and with reference to any of the specific Examples.

9. Vinyl chloride polymers and copolymers, whenever treated by the process according to any of claims 1 to 8.

10. Coatings and moulded articles, whenever prepared from a vinyl chloride polymer or copolymer according to claim 9.

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